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EFFECT OF METAL ADDITIVES AND THEIR BORIDES ON COMBUSTION RATE OF MIXED SYSTEMS

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Wright-Patterson Air Force Base, Ohio

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Block	Italic	Transliteration	Block	Italic	Transliteration
А а	*А а*	A, a	Р р	*Р р*	R, r
Б б	*Б б*	B, b	С с	*С с*	S, s
В в	*В в*	V, v	Т т	*Т т*	T, t
Г г	*Г г*	G, g	У у	*У у*	U, u
Д д	*Д д*	D, d	Ф ф	*Ф ф*	F, f
Е е	*Е е*	Ye, ye; E, e*	Х х	*Х х*	Kh, kh
Ж ж	*Ж ж*	Zh, zh	Ц ц	*Ц ц*	Ts, ts
З з	*З з*	Z, z	Ч ч	*Ч ч*	Ch, ch
И и	*И и*	I, i	Ш ш	*Ш ш*	Sh, sh
Й й	*Й й*	Y, y	Щ щ	*Щ щ*	Shch, shch
К к	*К к*	K, k	Ъ ъ	*Ъ ъ*	"
Л л	*Л л*	L, l	Ы ы	*Ы ы*	Y, y
М м	*М м*	M, m	Ь ь	*Ь ь*	'
Н н	*Н н*	N, n	Э э	*Э э*	E, e
О о	*О о*	O, o	Ю ю	*Ю ю*	Yu, yu
П п	*П п*	P, p	Я я	*Я я*	Ya, ya

* ye initially, after vowels, and after ъ, ь; e elsewhere. When written as ё in Russian, transliterate as yё or ё. The use of diacritical marks is preferred, but such marks may be omitted when expediency dictates.

FOLLOWING ARE THE CORRESPONDING RUSSIAN AND ENGLISH

DESIGNATIONS OF THE TRIGONOMETRIC FUNCTIONS

Russian	English
sin	sin
cos	cos
tg	tan
ctg	cot
sec	sec
cosec	csc
sh	sinh
ch	cosh
th	tanh
cth	coth
sch	sech
csch	csch
arc sin	$\sin^{-1}$
arc cos	$\cos^{-1}$
arc tg	$\tan^{-1}$
arc ctg	$\cot^{-1}$
arc sec	$\sec^{-1}$
arc cosec	$\csc^{-1}$
arc sh	$\sinh^{-1}$
arc ch	$\cosh^{-1}$
arc th	$\tanh^{-1}$
arc cth	$\coth^{-1}$
arc sch	sech^{-1}
arc csch	csch^{-1}

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rot	curl
lg	log

EFFECT OF METAL ADDITIVES AND THEIR BORIDES ON COMBUSTION RATE OF MIXED SYSTEMS

L. A. Romodanova and P. F. Pokhil
(Moscow)

We know that many metals which are added in small quantities to various compositions increase the combustion rate of the latter [1-5]. In order to ascertain the effect of molybdenum, zirconium, titanium, tungsten, iron, boron, and the borides of these metals (Table 1) on the combustion rate of mixed compositions the following stoichiometric compositions were prepared: oxidizer-ammonium perchlorate, fuel-methanoic acid and polymethylmethacrylate. The degree of dispersion in the ammonium perchlorate was <100 μ, 3 μ in the polymethylmethacrylate, and <50 μ in the methanoic acid.

The compositions were burned in a bomb (in a nitrogen atmosphere) and under the dome of a vacuum device. A photoregister was used to determine the combustion rate.

In order to study the effect of adding metals and their borides on the combustion process of mixed compositions in a vacuum ($p \approx 10^{-2}$ mm Hg) we use the combination of APC [ammonium perchlorate] +methanoic acid. The effect of the metals and their borides on the self-ignition temperature of APC and compositions based

on APC and fuels (dextrin, metal, naphthionic acid) was studied. The results of the experiment are shown in Tables 2 and 3.

Table 1. Some physicochemical properties of the metals and their borides [6].

(a) Металл и борид металла	(b) Дисперсность, μ	(c) Удельный вес, г/см³	(d) Температура плавления, °C	(e) Температура кипения, °C	(f) Температура самовоспламенения, °C
Fe	1	7,9	1539	2740	250
Zr	3	6,5	1900	5050	230
Б	6	2,3	2075	2550	460
W	19	19,3	3410	5930	450
Ti	6	4,5	1725	3260	510
Mo	4	10,3	2625	4800	380
FeB	2	6,71	1540	—	490
ZrB_2	5	6,04	3040	—	650
W_2B_5	2,5	13,1	2300	—	470
TiB_2	1,4	11,7	2950	—	480
Mo_2B_5	4	7,48	2100	—	355

Key: (a) Metal and metal boride; (b) Dispersion, μ; (c) Specific weight, g/cm^3; (d) Melting temperature, °C; (e) Boiling temperature, °C; (f) Self-igniting temperature, °C.

Table 2. Self-ignition temperature of sublimation and decomposition in a vacuum of APC with 2% addition of metals and borides.

Additive	Fe	Zr	B	Mo	Ti	W	FeB	ZrB	W_2B_5	TiB_2	Mo_2B_5
T,°C	356*	356*	356*	390**	390**	358*	390*	390*	390*	390*	390*

*Sublimation, decomposition.
**Sparks given off; sublimation, decomposition, partial ignition.

Table 3. Self-ignition temperature of compositions in vacuum, °C.

(a) Состав	(b) Без добавки металла	(c) С добавкой 2% металлов и боридов										
		Mo	Zr	W	B	Fe	Ti	Mo_2B_5	ZrB_2	W_2B_5	FeB	TiB_2
(d) ПХА+метаниловая кислота	330	290	290	290	360	290	330	320	360	340	320	330
(e) ПХА+декстрин	360	290	250	300	280	230	330	320	320	320	230	340
(f) ПХА+метол	360	240	270	330	360	300	340	300	340	330	360	350
(g) ПХА+нафтионовая кислота	450	380	420	310	410	450	450	380	450	450	390	360

Key: (a) Composition; (b) Without metal added; (c) With addition of 2% metals and boride; (d) APC+ +methanoic acid; (e) APC+dextrin; (f) APC+Metol; (g) APC+naphthionic acid.

In Table 2 we see that the addition of 2% molybdenum and titanium leads to partial ignition of the APC, while pure APC in a vacuum does not ignite (in air APC ignites at 380-420°C). Additions of other metals and their borides increase the sublimation and decomposition temperatures of APC (~300°C).

From the results shown in Table 3 it is apparent that all metal and metal boride additives reduce the self-igniting temperature of the APC+dextrin combination. The self-igniting temperature of APC+naphthionic acid and APC+Metol either remains unchanged under the effect of the additives and their borides or declines. The self-igniting temperature of APC+methanoic acid with such additives as B, ZrB_2, and W_2B_5 even increases somewhat, while the other additives decrease the self-igniting temperature of the composition.

We measured the combustion rate of APC+methanoic acid and APC+dextrin with 2% additions of iron, zirconium, boron, molybdenum, titanium, tungsten and their borides in a vacuum ($p \sim 10^{-2}$ mm Hg, preheating ~200°C). The results of the experiments are shown in Table 4.

Table 4. Combustion rate of compositions in a vacuum, cm/s.

(a) Состав	(b) Без добавки	(c) С добавкой металлов или боридов										
		Mo	Zr	Fe	W	Ti	B	Mo_2B_5	ZrB_2	FeB	W_2B_5	TiB_2
(d) ПХА+метанилловая кислота	0,0124	0,0965*	0,0250	0,0193	0,0183	0,0175	0,0138	0,0390*	0,0216	0,0290	0,0240	0,0360
(e) ПХА+декстрин**	0,0200	—	—	—	—	—	—	0,0210	0,0160	0,0265	0,0210	0,0186

*Burns without preheating.
**Combustion unsteady.
Key: (a) Composition; (b) Without additives; (c) With metal or boride additives; (d) APC+methanoic acid; (e) APC+dextrin.

With additions of metals Mo, Zr, Fe, W, Ti, and B the combination of APC+dextrin burns more steadily than when the borides of these metals are added. As we see in Table 4, most effective for APC+methanoic acid burning in a vacuum are additions of molybdenum and molybdenum boride. The first increases the combustion rate of the composition more than 8 times, the second- more than 3 times. The addition of metal borides increases the combustion rate of APC+methanoic acid in a vacuum from 1.8 to 3 times.

Figures 1 and 2 show the results of measuring the combustion rate of APC+methanoic acid with metals added in a pressure range of 10-100 kgf/cm^2. From these diagrams we see than additions of molybdenum, titanium, and tungsten increase the combustion rate of APC+methanoic acid in the high-pressure range, beginning at 40 kgf/cm^2. Thus, at a pressure of 100 kgf/cm^2 the combustion rate of the composition with molybdenum added is almost 1.3 times greater than the combustion rate of this composition without the additives. In the low-pressure range (10-40 kgf/cm^2) the effect of the additives is very weak. In this pressure range the iron additive is the most effective. Thus, at a pressure of 20 kgf/cm^2 the combustion rate of the composition with the additives is 1.4 times greater than the combustion rate without the additives.

In the high-pressure range (60-100 kgf/cm^2) additions of iron, zirconium, and boron have a considerably weaker effect.

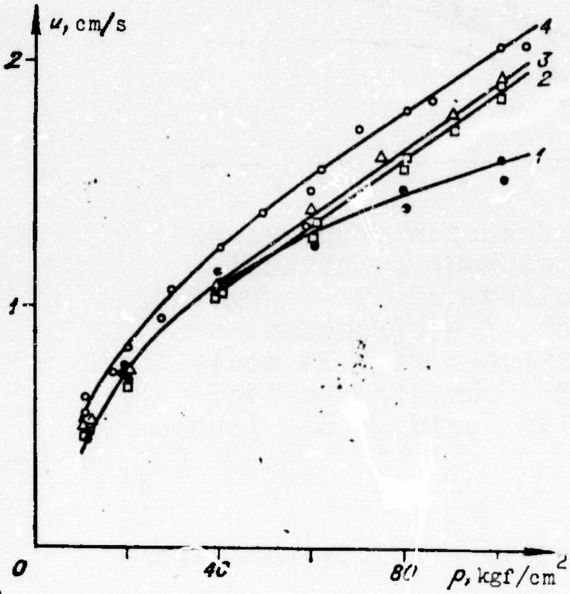

Figure 1

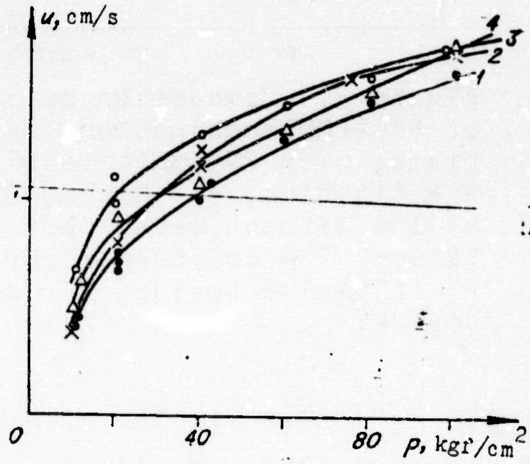

Figure 2

Figure 1. Combustion rate as a function of pressure of combination APC+methanoic acid without additives (1) and with a 2% addition of tungsten (2), titanium (3), and molybdenum (4).

Figure 2. Combustion rate as a function of pressure of combination APC+methanoic acid without additives (1) and with 2% boron (2), iron (3), and zirconium (4).

Figure 3 shows the results of determining the combustion rate of APC+polymethylmethacrylate with metal additives. It is apparent from this diagram that all metals increase the combustion rate of the composition. Adding 2% molybdenum not only increases the combustion rate of the composition in a pressure range of 10 kgf/cm^2-60 kgf/cm^2, but also changes the dependence of composition on pressure: the combustion rate of the composition with 2% Mo added does not depend on pressure in the pressure range of 10-100 kgf/cm^2. Iron increases the combustion rate of the composition ~1.8 times at a pressure of 20 kgf/cm^2 and 2 times

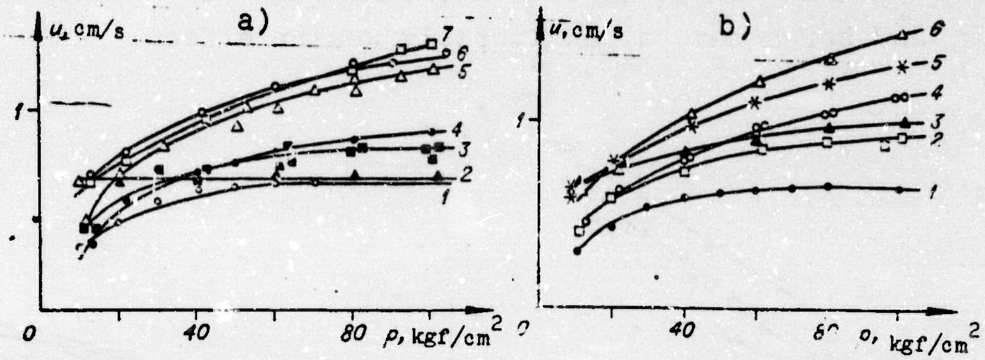

Figure 3. Combustion rate as a function of pressure of PAC+PMM combination. a) 1 - without metal additives; with 2% additives; 2 - molybdenum, 3 - tungsten, 4 - titanium, 5 - boron, 6 - iron, 7 - zirconium. b) 1 - without metal boride additives; with 2% additives: 2 - molybdenum boride, 3 - tungsten boride, 4 - titanium boride, 5 - zirconium boride, 6 - iron boride.

at p=100 kgf/cm^2. Similar with respect to effectiveness are zirconium and boron additives. The effect of titanium, tungsten, and molybdenum (at p>20 kgf/cm^2) is weaker. If we compare the effect of the metal additives on the combustion rate of APC+PMM [polymethylmethacrylate] and APC+methanoic acid under pressure, then we come to the conclusion that the most effective in this case is iron. This is apparently related to the fact that iron is the catalyst of the combustion processes.

As demonstrated by the experiments, the effect of adding Mo, Zr, Ti, and W on the combustion rate of mixed compositions was more effective in a vacuum. This seems to be related to the intense contamination of these metals by adsorbed gases (O_2, N_2, and others) in air.

Zirconium, titanium, tungsten, and their oxides have catalytic properties in the processes of hydriding, hydrogenation, hydrocracking, dehydrogenation, dehydriding, polymerization reactions, and also, as the studies showed, in the processes of combustion. In some processes these metals can be catalysts

proper, in others - activators or carriers. Adding metal borides (Fig. 3b) increases the combustion rate of APC+PMM over the entire studied range in pressures 10-120 kgf/cm^2. The greatest increase in the combustion rate of APC+PMM is observed when iron boride is added, which at a pressure of 20 kgf/cm^2 increases the combustion rate of the composition 1.7 times and 2.2 times at 100 kgf/cm^2.

Of the studied metals molybdenum has the most interesting properties [7, 8]. The oxidizability of molybdenum depends on the length of the process, temperature, and oxygen pressure. At a temperature below 500°C oxidation occurs according to the parabolic law, which indicates partial formation of a protective film. Oxidation of molybdenum occurs in two stages with the formation of an intermediate molybdenum dioxide layer and an outer layer of molybdenum trioxide:

$$Mo \longrightarrow MoO_2 \longrightarrow MoO_3.$$

The molybdenum trioxide which is formed during the oxidation process is an excellent catalyst of combustion processes. When heated above 500°C it begins to volatilize. At 770°C the evaporation rate of MoO_3 is equal to its formation rate, and with further heating the rate of volatilization increases rapidly. The final oxidation rate of molybdenum is a linear function of time (this indicates that no protective film is formed), and the rate of reaction is determined by the oxidation rate of the molvbdenum dioxide to trioxide.

At temperatures below the melting point of molybdenum trioxide (795°C) the oxidation mechanism consists of oxygen diffusion into the metal through scale, as a result of which oxidation occurs on the oxide-metal interface. This phenomenon is rather unusual, since in most cases oxidation of metals and alloys occurs through the diffusion of the metal ions out through the scale [skin] layer, and oxidation occurs between the oxide and the atmosphere.

The presence of molten molybdenum trioxide at temperatures above 815°C accelerates oxidation catastrophically, and it occurs rapidly as a result of the flowing of the liquid oxide over the surface. The oxygen is diffused through the liquid phase at a high rate. The oxidation rate of the molybdenum at 980°C can be less than at 815°C, since at the higher temperature the evaporation rate of the trioxide increases so much that the liquid oxide loses contact with the metal.

The molybdenum properties above help to explain the effectiveness of molybdenum as an additive to mixed compositions burning in a vacuum and also its unique effect on the nature of the dependence between combustion rate and pressure for the combination of polymethylmethacrylate and ammonium perchlorate in the pressure range of 10-100 kgf/cm^2. When additives are introduced into a mixed fuel composition their first effect is felt in the condensed phase, where there occurs an intensification in the interaction of decomposition products, and this leads to an increase in the rate of heat liberation in the k-phase. The subsequent effect of the additives on the condensed and gas phases is to substantially change the combustion patterns of mixed systems. The best additives for increasing the combustion rate of mixed compositions in a vacuum are molybdenum, titanium, and their borides.

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